MOMEC97

Molecular Modeling

Peter Comba, Trevor W. Hambley, Gilbert Lauer
and Norbert Okon

User's Guide

Copyright © Dr. Gilbert Lauer / Dr. Norbert Okon
Chemische Verfahrens- & Softwareentwicklung (CVS) Heidelberg

All Rights Reserved

No part of this publication may be copied or replicated in any form without the written permission of CVS.

CVS makes no warranties, either expressed or implied warranties of merchantability or fitness for a particular purpose, regarding these materials and makes such materials available solely on an "as-is" basis.

In no event shall CVS be liable to anyone for special, collateral, incidental, or consequential damages in connection with arising out of purchase or use of these materials. The sole and exclusive liability to CVS, regardless of the form of action, shall not exceed the purchase price of the materials described herein.

Third party trademarks

Microsoft, Windows, Windows NT are registered trademarks of Microsoft Corporation.
HyperChem is a registered trademarks of Hypercube, Inc.

All other brand and product names are trademarks or registered trademarks of their respective holders.

Printed in Germany 1997

Authors

Prof. Peter Comba	Anorganisch-Chemisches Institut, Universität Heidelberg, Germany
Dr. Trevor W. Hambley	School of Chemistry, University of Sydney, Australia
Dr. Gilbert Lauer	Anorganisch-Chemisches Institut, Universität Heidelberg, Germany
Dr. Norbert Okon	Anorganisch-Chemisches Institut, Universität Heidelberg, Germany

e-mail: momec@akcomba.oci.uni-heidelberg.de

Preface

Molecular mechanics (MM) is a technique that is widely used for the computation of molecular structures and relative stabilities. The advantages of MM over quantum chemical methods are mainly due to the computational simplicity of empirical force field calculations, which leads to a comparatively small computational effort for MM calculations. Therefore, even large molecular assemblies can be studied using MM, and energy surfaces with many minima can be screened and mapped successfully.

MM has been used routinely for many years in the area of organic chemistry. Studies on inorganic systems have been less common until recently. Effects of variable coordination numbers, oxidation and spin states and electronic influences resulting from partly filled d-subshells have been difficult to model with conventional MM approaches. *MOMEC97* has been developed for inorganic compounds and offers a variety of functional forms and force field parameters that allow organic and inorganic chemists alike to solve both conventional and more specialized problems. A series of additional modules has been designed to allow *MOMEC97* to be applied to a variety of problems such as the computation of isomer distributions, the calculation of rotational energy barriers and the determination of metal ion selectivities of ligand systems.

MM is an empirical method, and it is important for the evaluation of a possible application of MM to a particular problem and for the interpretation of the results to be aware of the theoretical basis and the type of parameterization used. The *MOMEC97* manual provides you with the functional forms and parameters implemented in the program, and it demonstrates how you can choose and modify the functions and parameters. However, it does not dwell on theory, parameter development and possible applications of the various techniques. These are covered in the original literature. For a recent comprehensive account of both the general theory and applications of MM, especially in the field of inorganic chemistry, we refer to our recently published book (Peter Comba and Trevor W. Hambley "Molecular Modeling of Inorganic Compounds" VCH, 1995). Also, we have published a tutorial on

molecular modeling of inorganic compounds, based on *MOMEC97* (Peter Comba and Trevor W. Hambley "Molecular Mechanics of Inorganic Compounds" Tutorials in Computational Chemistry, Science Learning Ltd, 1997, info@scienceserve.com).

June 1997

Peter Comba
Gilbert Lauer
Trevor W. Hambley
Norbert Okon

Contents

Preface 3
Contents 5
Introduction 7
What is *MOMEC97*? 7
What is Provided? 8
System Requirements 9
Getting Started 10
Description of *MOMEC97* 12
Using *MOMEC97* 14
Opening a *MOMEC97* session 14
The *MOMEC97* menus: 14
File 14
  Open Session 14
  Save Session as 14
  Print 14
  Exit 15
Edit/View 16
  Summary File 16
  Result File 18
  Log File 18
  HyperChem File 18
  Listing Files 18
  Force Field 19
  Interaction Array 20
Parameter Array 21
  Batch-Job 22
  Batch-Job Results 22
Execute 24
Additional Modules 24
Conversion 24
Structure 25
Energy 27
Intersection 30
Rigid Geometry 31
  Fixed Atoms 31
  Fixed Shell 32
Jahn-Teller 33

Setup 36
Files 36
Force Field 37
Listing 37
Optimization Controls 38
Algorithm 38
Interactions 39
Termination Conditions 39
Other Conditions 39
Tools 41
Sort Atoms 41
Set Metal Atom Type 41
Delete H-Atoms 42
Build Interactions 42
Build Selections 42
Delete Selections 43
Switch Atom Types 43
- to MOMEC97 types 43
- to HyperChem types 43

Appendix A: Potential Energy Functions, Force Fields, Atom Types 44
Potential Energy Functions 44
Force Field Files 46
Appendix A: 49
Atom types used in MOMEC97 49
Appendix B: 56
Technical Details of the Opening Precedure of MOMEC97 56
Appendix C: 58
Tutorial 58
Building and refining a simple metal complex: $[Co(NH_3)_6]^{3+}$ 58
Appendix D: 61
The Plane Twist Function 61

Introduction

What is *MOMEC97*?

MOMEC97 is a molecular mechanics system that has been developed for strain energy minimization of metal complexes. It operates in a Microsoft Windows environment and it is designed to be used in conjunction with *HyperChem*. It has a number of features that facilitate its application to a wide variety of problems and that are not available in many other molecular mechanics programs.

MOMEC97 offers:

- Graphical input and output through *HyperChem*
- A choice of either conjugate-gradients or full-matrix Newton-Raphson refinement or a combination using both methods
- True constraints of internal coordinates
- Selective inclusion of 1,3-interactions
- Modeling of coordination geometries by either intraligand repulsion, electrostatic interactions, ligand field based electronic functions or a combination of various methods
- A plane twist-angle function
- A rigid geometry module for pre-refinement and for macro-molecules
- An existing extensive force field for transition metal and rare earth compounds
- An editor for force field parameters and data files
- Execution of batch jobs
- A module for the refinement of Jahn-Teller distorted hexa-coordinate compounds
- A module for the computation of torsional barriers and ligand hole sizes
- An interface to the file conversion program *Babel*
- A module for the calculation of relevant structural parameters, such as best planes, angles between planes and lines, twist angles etc.

What is Provided?

MOMEC97 is a program that operates in a Microsoft Windows environment. It accepts input from *HyperChem* and produces output readable by *HyperChem*. *MOMEC97* has a Windows interface that can be used to set up and modify the *MOMEC97* control files, to modify force field parameters, coordinates and atom types, to run *MOMEC97* either interactively, in the background or as a batch job, to look at a summary of any *MOMEC97* run and examine errors that occurred during the strain energy minimization, to run various other modules that are available for the use in conjunction with *MOMEC97,* and to launch *HyperChem* with the most recently minimized structure in the workspace.

Additional modules available for applications in conjunction with *MOMEC97* and/or *HyperChem* include *Structure* (calculation of structural parameters that are not available in *HyperChem*), *Jahn-Teller* (structural optimization of Jahn-Teller distorted hexacoordinate compounds)*, Energy* (computation of the strain energy as a function of constrained internal coordinates), *Conversion* (an interface to the freeware program *Babel* which converts coordinate files to and from various formats) and the *Rigid Geometry* module to minimize parts of molecules.

The installation program creates the new directory \momec97 and copies executable and control files to this directory. It also creates the subdirectories \momec97\parm, and \momec97\example. In addition, the installation program creates a directory \momtypes in the *HyperChem* path where the original *HyperChem* files chem.rul, typerule.bin and ambertyp.txt and the corresponding *MOMEC97* files are stored. These are necessary for communication between *MOMEC97* and *HyperChem*. The original *HyperChem* files have the extensions *.hyp and those of *MOMEC97* have the extensions *.mom. *MOMEC97* switches between these files and after each session the original *HyperChem* files are restored.

System Requirements

To run *MOMEC97,* you need a 486 processor (with maths coprocessor) or higher system with at least 640 K of memory, Windows95 or WINDOWS NT 4.0. Less than 6 M of disk space is required to install all files. To make use of *MOMEC97* in conjunction with *HyperChem*, *HyperChem* 3.0 or higher is required. For *MOMEC-HyperChem* it is necessary to have 8 M or more of memory.

Getting Started

Installation

1. Place the program disk in your floppy drive

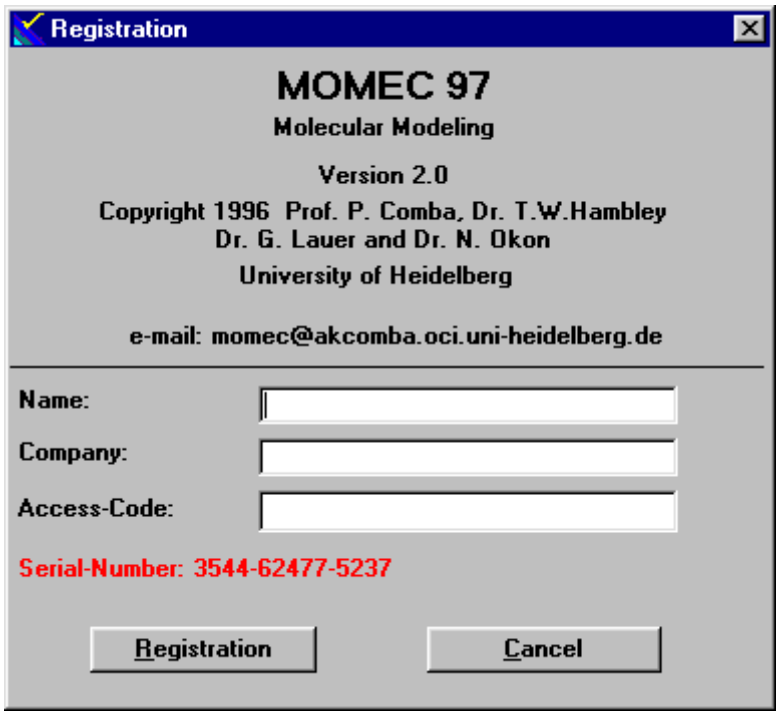
2. Click on Start in the Taskbar of Windows95 and choose Run.
The Run dialog box opens.
Enter the following command in the open text box:

a:\setup or
b:\setup

depending on which drive you are using.

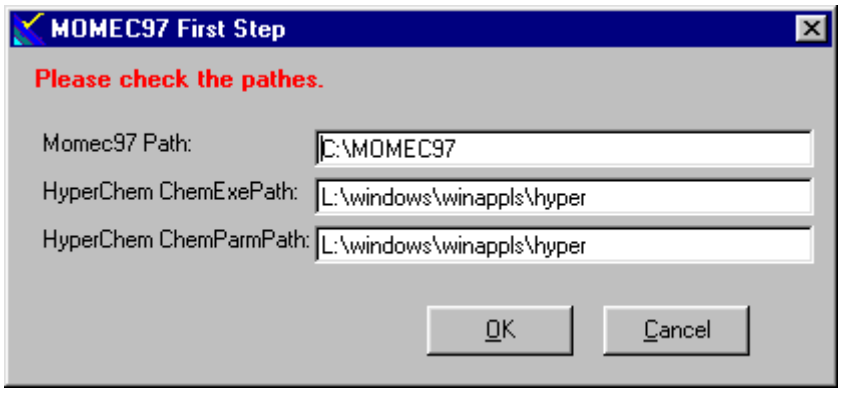
3. Choose OK.

When you start *MOMEC97* for the first time the following dialog box appears:



Send the Serial-Number that appears to your *MOMEC97* dealer to get the Access-Code.

When you enter the correct Access-Code the following dialog box appears:



Check the paths and then click on the OK button.

Note:

MOMEC97 uses a point for decimal values (e.g. 0.01 and not 0,01). Thus, you should set the decimal point in your *WINDOWS* settings.

Description of *MOMEC97*

MOMEC97 is a program for strain energy minimization. It was developed for use in the modeling of transition metal compounds but can be used in any area of chemistry. Minimization is achieved by either conjugate-gradients (first-derivative) refinement, full-matrix Newton-Raphson (second-derivative) refinement or by a combination using both minimizers.

Most energy minimization programs rely on variants of what are called 'first-derivative' techniques to achieve energy minimization. The most commonly used technique is called 'conjugate gradients'. The advantage of these techniques is their modest memory requirements and ability to cope with crude starting models. A disadvantage is that the convergence criterion is based on the rate of change of the strain energy. It is not possible to verify whether a true minimum has been reached, and convergence can occur at some distance away from the minimum. 'Second-derivative' methods such as the Newton-Raphson method yield mathematically verifiable minima and generally do so after far fewer iterations. Also, it is possible with second-derivative methods to impose mathematically precise constraints; in first-derivative methods only restraints are available. The disadvantages of second-derivative methods are their large memory requirements and the need to have a good starting model. In some cases second-derivative methods will converge at a saddle point, where one of the second derivatives is positive rather than negative.

The conjugate-gradient Fletcher-Reeves method is superior if structures far away from the energy minimum are to be minimized. Therefore, it is suggested that this algorithm be used when starting with a crude model. The precise definition of the energy minimum requires the calculation of the second derivatives. Therefore, it is advisable to switch to the Newton-Raphson minimizer in the final cycles of the structure optimization.

Molecular modeling of metal complexes is not as precise a science as is modeling of simple organic compounds. However, it is capable of yielding useful and informative results. The major impediment to

achieving successful modeling of metal complexes is the degree of variability found. Most metals can adopt a number of oxidation states, coordination numbers and coordination geometries. Also, there is frequently an interplay between steric and electronic factors that runs contrary to the underlying philosophy of molecular mechanics. In order to facilitate the modeling *MOMEC97* has been designed to have maximum flexibility. All force field parameters are external to the program and can be readily modified with the force field editor from the *MOMEC97* window. Also, *MOMEC97* offers a number of different approaches to the modeling of coordination geometries. These include points on a sphere models with 1,3-nonbonded or electrostatic interactions or various angle potentials including multiple harmonic and plane twist functions.

Using *MOMEC97*

Opening a *MOMEC97* session

MOMEC97 uses modified *AMBER* atom types (see Appendix A). Therefore, when you start *MOMEC97* the typrule.bin, ambertyp.txt and chem.rul files in the *HyperChem* directory are automatically modified. For that reason, we recommend that as a first step you always open *MOMEC97*, even if your first task is to view or build a molecule. You may then open *HyperChem* from the *MOMEC97* window with the menu item *Execute / HyperChem*. After exiting *MOMEC97* the original *HyperChem* atom type files will be restored. You can also switch between the two types (see *MOMEC97* Tools), and this may be useful if you want to use specific *HyperChem* tools (data bases, molecular dynamics, quantum chemical calculations) during a *MOMEC97* session (an example of internal automatic file transfers is given in Appendix B).

The *MOMEC97* menus:

File

Open Session

MOMEC97 generally starts with default parameters for many of the menu items and control parameters that are explained below. These are given in the momec.ini file. The Open Session command allows you to use parameters from an earlier session if you have saved it. The extension of these files are *.ini, and you can see the name of the ini file that you are using in the header of the *MOMEC97* window.

Save Session as

Here you can save the session parameters in a *.ini file. The default file is momec.ini.

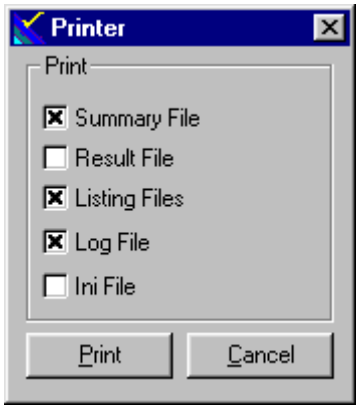
Print

This command allows you to print various result files. A mouse click on the Print button opens a window from which you may choose the files that you want to print. If you choose the item Listing Files all items that

have been checked in the window Setup / Listing (see below) will be sent to the printer.

Note:

The Result File can be very long (100 or more pages).



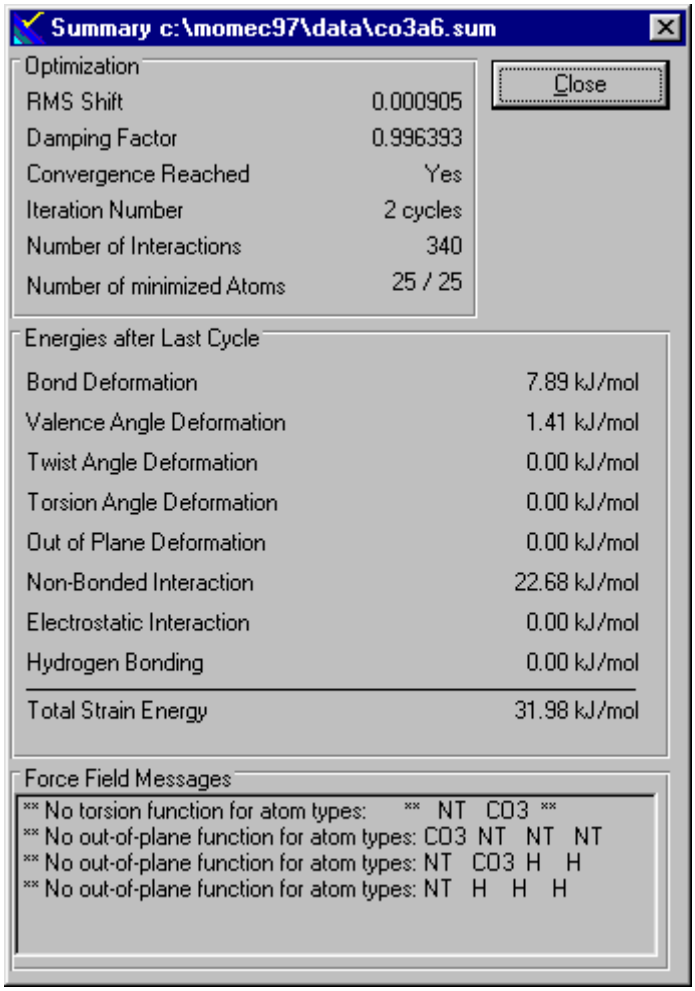
Exit

Quits the *MOMEC97* session.

Edit/View

Summary File

The summary file reports all relevant parameters. This window reports the final data following termination of the calculation but you may have chosen to refresh it after any number of cycles (see Optimization Controls). You may only view the final Summary file of an earlier calculation if you have saved the corresponding result file (see Setup Files).


Summary c:\momec97\data\co3a6.sum
Optimization
Close
RMS Shift 0.000905
Damping Factor 0.996393
Convergence Reached Yes
Iteration Number 2 cycles
Number of Interactions 340
Number of minimized Atoms 25 / 25
Energies after Last Cycle
Bond Deformation 7.89 kJ/mol
Valence Angle Deformation 1.41 kJ/mol
Twist Angle Deformation 0.00 kJ/mol
Torsion Angle Deformation 0.00 kJ/mol
Out of Plane Deformation 0.00 kJ/mol
Non-Bonded Interaction 22.68 kJ/mol
Electrostatic Interaction 0.00 kJ/mol
Hydrogen Bonding 0.00 kJ/mol
Total Strain Energy 31.98 kJ/mol
Force Field Messages
** No torsion function for atom types: ** NT CO3 **
** No out-of-plane function for atom types: CO3 NT NT NT
** No out-of-plane function for atom types: NT CO3 H H
** No out-of-plane function for atom types: NT H H H

If the ***RMS shift*** (root mean square shift) after a cycle is less than the value you have chosen in the window *Setup / Optimization Controls*, the calculation stops.

Note:
This field is only active with the full-matrix Newton-Raphson minimizer.

The ***Damping Factor*** field reports the effective damping factor.

The ***Convergence Reached*** field shows whether your optimization is finished. If your minimization method is the full-matrix Newton-Raphson algorithm, the convergence criterion is the RMS shift that you have chosen in the Optimization Controls menu. If your algorithm is the Conjugate-Gradient minimizer, the convergence criterion is reached when the difference between the energies of the last two cycles is less than one percent.

The field ***Iteration Number*** shows the current number of iterations. If convergence has not been achieved, the Iteration Number shown corresponds to the maximum number of cycles that you had chosen in the menu item *Setup / Optimization Controls* as a termination criterion.

The field ***Number of Interactions*** indicates how many interactions have been used to calculate the total strain energy. This may be a very large number and this contributes to the CPU time and amount of memory needed for the calculation. You can reduce the number of interactions by reducing the value for the Search Limit (cutoff for the van der Waals interactions) in the window *Setup / Optimization Control*. Also, this value will be reduced in the Rigid Geometry mode.

The field ***Number of Minimized Atoms*** indicates how many atoms are shifted during the minimization procedure. Usually this corresponds to the number of atoms in the refined molecule, e.g. 25/25 for a 25 atom species. In the Rigid Geometry mode the number of refined atoms is reduced, e.g. 15/25. In this case the 10 atoms that are not refined do not contribute to the total strain energy.

The information ***Energies after Last Cycle*** lists all potential energy terms. Potentials that have not been activated in *the Setup / Optimization Controls* menu are recorded as zero energy contributions.

In the field ***Force Field Messages*** *MOMEC97* gives you information of interaction types that could not be included because the relevant force field parameters were missing from the files.

Note:

This is not necessarily an error message since for some interactions you may not want to define a potential. However, it is good practice to carefully check this list.

Result File

The Result File contains all interaction parameters (distances, angles etc. and corresponding energies) and a summary of energies for each cycle. Exceedingly high energies for specific interactions are marked with one to six asterisks (*), depending on the amount of the energy involved.

Note:

The Result File can be very large.

Log File

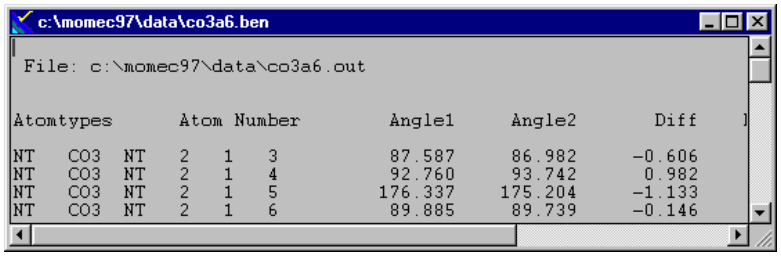
The *Log File* is a record of the computation. It has information on the cartesian coordinates of each atom and their shifts. The file also indicates the last steps before an abnormal termination.

HyperChem File

Here you can view and edit the currently active *HyperChem* input file (the names and extensions are given in the *Setup / Files* menu; input files usually have the extension *.hin while output files have the extension *.out).

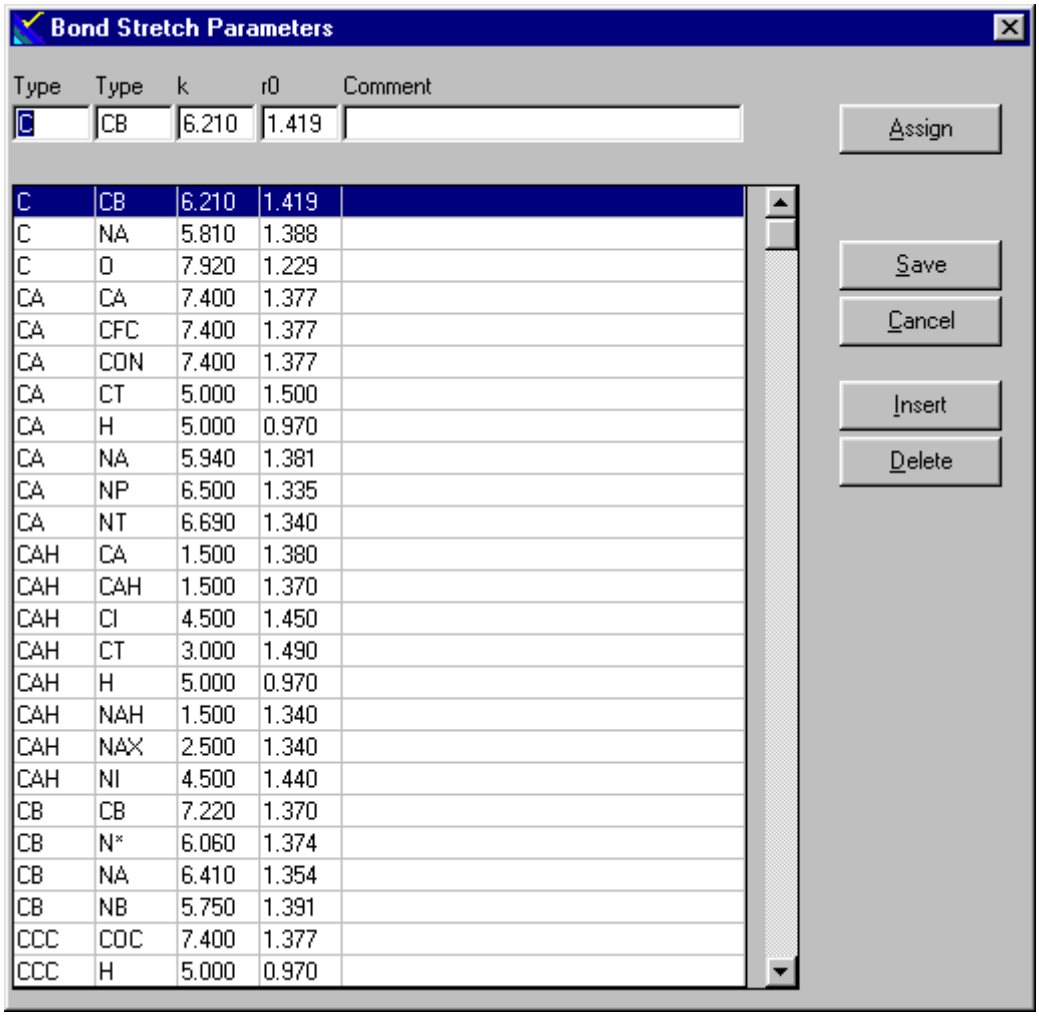
Listing Files

Each of these files is produced and saved if (i) the corresponding interactions are activated in the *Setup / Optimization Controls* menu and (ii) if the corresponding box in the *Setup / Listing* is checked. All Files have the same format. They also give differences between the starting and the final value of the corresponding structural parameter and the strain energy involved. Note that the "starting value" is that of the last Result Refresh Period *(Setup / Optimization Controls)*, i.e. it only corresponds to the initial structure if that parameter value is set to zero. The example shows a section of a valence angles listing file.


c:\momec97\data\co3a6.ben
File: c:\momec97\data\co3a6.out
Atomtypes Atom Number Angle1 Angle2 Diff
NT CO3 NT 2 1 3 87.587 86.982 -0.606
NT CO3 NT 2 1 4 92.760 93.742 0.982
NT CO3 NT 2 1 5 176.337 175.204 -1.133
NT CO3 NT 2 1 6 89.885 89.739 -0.146

Force Field

With this menu item you can open the force field editor. The example shows Bond Stretch Parameters.



Click with the mouse on the line in the table that you want to edit and change the parameter values for that interaction in the editing box at the top of the page. The *Assign* button modifies the parameters in the table and therefore in the parameter field. *Save* quits the editor with all changes saved to the corresponding file. You may also insert new

interaction types with the *Insert* button or delete an interaction with the *Delete* button.

Interaction Array

The interaction array is a temporary file that is derived from the coordinate input file (*.hin) and the force field. Together with the Parameter Array it assembles the information that is necessary to calculate all the terms for the total strain energy. It is possible to edit and save this file, and that can be useful for advanced applications. This array has the following form:

Interaction name	atom number	atom number	atom number	atom number	atom number	index to parameter array 1	index to parameter array 2
TYP	1	0	0	0	0	0	0
TYP	2	0	0	0	0	1	0
STR	**1**	**2**	**0**	**0**	**0**	**0**	**0**
STR	1	3	0	0	0	0	0
STR	2	8	0	0	0	1	0
BEN	2	1	3	0	0	0	0
BEN	1	2	8	0	0	1	0
NBD	8	13	0	0	0	2	1

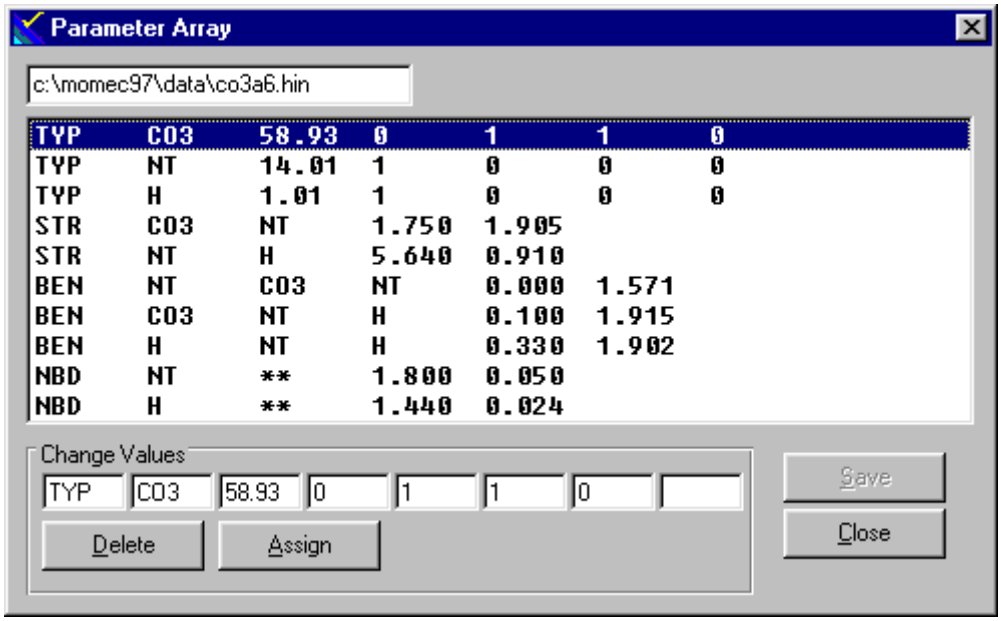
The last two columns are the code to the force field parameters of the molecule, which have been copied from the force field files to the parameter array. For example, **STR 1 2 0 0 0 0 0** points to the values of 0.600 for the force constant and 1.970 for the equilibrium distance (see parameter array below). Thus, the bond stretch interaction between atom number 1 (CU2) and atom number 2 (NT) is calculated with these parameter values.

Parameter Array

The force field parameters that are needed in the current calculation are assembled in a temporary file of the form:

Interaction name	atom type 1	atom type 2	atom type 3	value 1	value 2
TYP	CU2			63.546	
TYP	NT			14.007	
STR	**CU2**	**NT**		**0.600**	**1.970**
STR	NT	H		5.640	0.910
BEN	NT	CU2	NT	0.030	1.571
BEN	CU2	NT	H	0.100	1.915
NBD	NT	**		1.800	0.050
NBD	H	**		1.440	0.024

This file may also be edited and saved *(Edit/View / Parameter Array)*



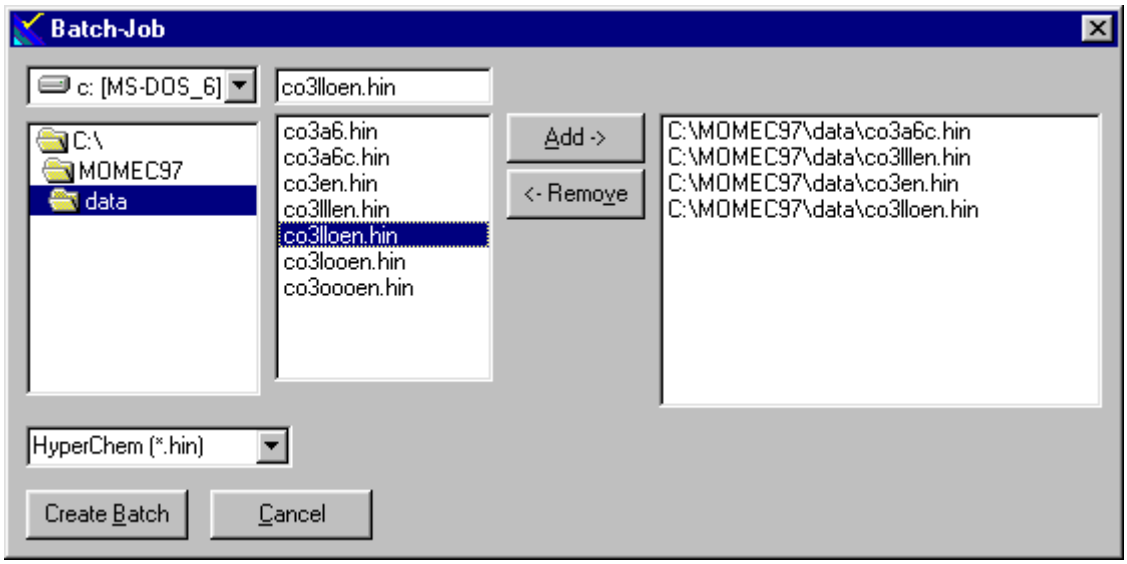
Select the line that you want to modify. Change the parameters in the box for the changes, activate the changes with the *Assign* button and *Save* the edited file.

The Interaction Array and Parameter Array files can be useful for quick changes to the force field (e.g. for the development of new force field parameters). The first step is to set up these files: use the menu item *Tools / Build interaction* to create the two files (note that at the start of each optimization these two files are built but they are not available for editing unless you build them with *Tools / Build interaction*). Edit the

parameter array using the menu item *Edit/View / Parameter Array*. Set the option button *Use interaction and parameter files* in the *Setup / Optimization Controls* to *Yes*. Calculate the structure using the menu item *Execute / Geometry Calculation*. Check the results (Summary, Listing Files). Change the parameter, refine again and note the changes in energy and structure.

Batch-Job

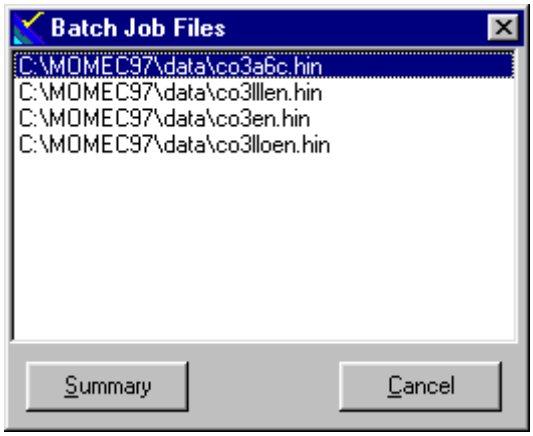
This mode is used to energy minimize a series of molecules. You can prepare the batch job with the menu item *Edit/View / Batch-Job*. A window appears, which allows you to choose the structures that you want to refine. Select the files, confirm your choice with a mouse click on the *Create Batch* button and save the file with a file name and directory of your choice.



To start a batch-job go to the window *Execute / Batch-Job*. For each of the files in the batch-job the same Control Parameters apply *(Setup / Optimization Controls)*. The usual output files are created, i.e. Name.OUT (refined coordinates), Name.RES (the result files), Name.SUM (the summary files) and the listing files that you have selected with the menu item *Setup Listing*.

Batch-Job Results

This item helps you to browse through the results of batch-jobs. You first have to select the name of the batch-job that you want to analyze. Then a standard dialog box with the following window appears:



The required results are displayed if you select a structure file from the list and then click the *Summary* button or double click on a file in the box. The results will be listed in the Summary window.

Execute

Geometry Optimization

This button starts the refinement of the molecule specified in *Setup / Files / Input* using the parameters specified in *Setup / Force Field*, *Setup / Optimization Controls* and, when the option *Use Interaction and Parameter Files* has been chosen in the *Setup / Files* menu, the edit *Interaction Array* and the *Parameter Array* present in the *Edit/View* window. As a result you will see the *Summary* file discussed above and, if the *Refresh Period* in *Setup / Optimization Controls* is set to a value different from zero, the refined molecule will be displayed in the *HyperChem* window. Also, the listing files that you have checked in *Setup / Listing* will be created.

HyperChem

This menu item allows *HyperChem* to be opened with either the *Input* or the *Output* file specified in *Setup / Files* displayed. Use this button if you need *HyperChem* during a *MOMEC97* session (e.g. if you want to build a new molecule). *HyperChem* then uses the *MOMEC97* atom types.

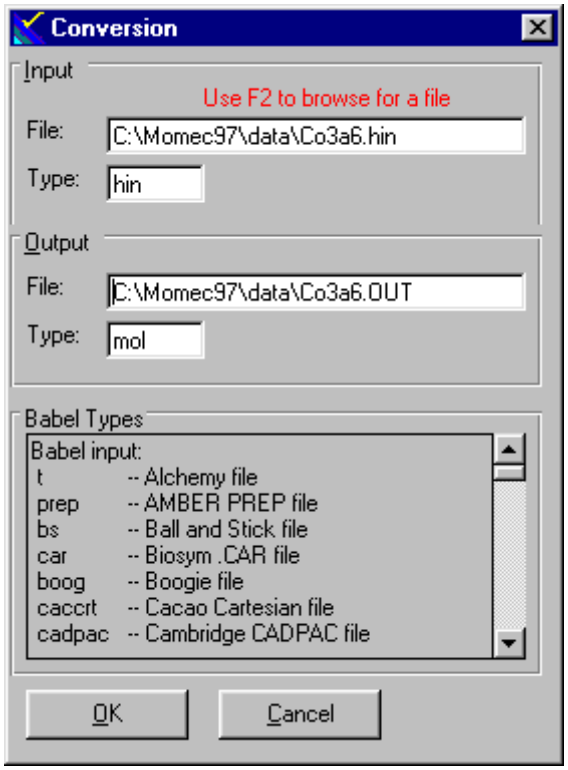
Batch-Job

A mouse click on this button opens a standard dialog box from which you open a batch-job that you have prepared in *Edit/View / Batch-Job*. The refinement starts with a mouse click on *Open*.

Additional Modules

Conversion

Conversion is a tool that facilitates use of the public domain program *Babel* from Windows without using a DOS-Prompt. *Babel* can be ordered from the e-mail address, babel@mercury.aichem.arizona.edu. Input and output files are specified in the appropriate *File* boxes. The type of the input files and type of required output file are indicated in the corresponding *Type* boxes. Clicking on *OK* initiates the *Babel* conversion.

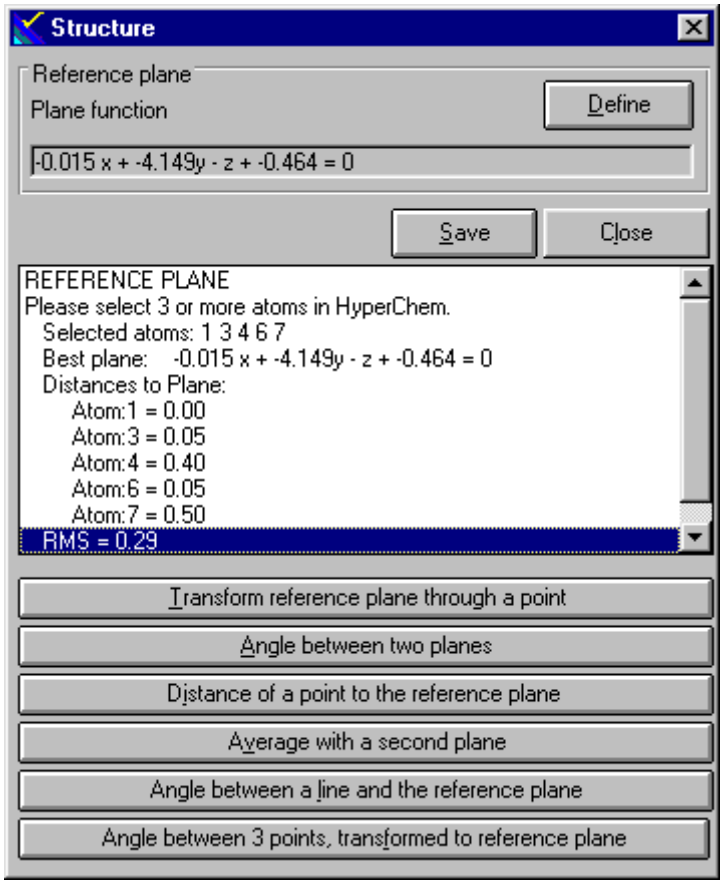


The list shows you the types that are supported by *Babel*.

Structure

The Structure tool allows for the calculation of some geometrical parameters that are not available from within *HyperChem*. Common to all of these evaluations is a reference plane. To use *Structure* open the menu item *Execute / Structure*. Click the button *Define* and select in *HyperChem* three or more atoms for the reference plane (if you have not opened *HyperChem* before it will open automatically; the molecule displayed and used in *Structure* will always be that defined as the *Input* in *Setup / Files*). When you use only three atoms, the plane will be exact. When you have chosen more than three atoms the program will calculate the best plane based on minimizing the sum of the squares of the distances of the atoms from the plane (least-squares plane).

After you have clicked the *OK*-button, the equation defining the plane is reported and if you have chosen more then three atoms, the list of the distances from each selected atom to the plane and the RMS shift are also given.


Structure
Reference plane
Plane function
Define
-0.015 x + -4.149y - z + -0.464 = 0
Save
Close
REFERENCE PLANE
Please select 3 or more atoms in HyperChem.
Selected atoms: 1 3 4 6 7
Best plane: -0.015 x + -4.149y - z + -0.464 = 0
Distances to Plane:
Atom:1 = 0.00
Atom:3 = 0.05
Atom:4 = 0.40
Atom:6 = 0.05
Atom:7 = 0.50
RMS = 0.29
Transform reference plane through a point
Angle between two planes
Distance of a point to the reference plane
Average with a second plane
Angle between a line and the reference plane
Angle between 3 points, transformed to reference plane

The button *Transform reference plane through a point* moves the reference plane to one that is parallel but passes through the selected atom. The resultant plane is the new reference plane.

The button *Angle between two planes* requires you to select three or more atoms in *HyperChem* to define a new plane. The list field shows the angle between the reference plane and the new plane.

The button *Distance from a point to the reference plane* asks you to select an atom in *HyperChem*. The list file shows the distance from the selected atom to the reference plane.

The button *Average with a second plane* requires you to select three or more atoms in *HyperChem* for a new plane. The list field shows the plane function which results from the average of the reference plane and the new plane. It also shows the intersection of the average plane with

the axis of the coordination system The resultant average plane is the new reference plane.

The button *Angle between a line and a reference plane* asks you to select two atoms in *HyperChem*. The list field shows the angle between the line through these two atoms and the reference plane.

The button *Angle between 3 points, transformed to reference plane* asks you to choose three atoms in *HyperChem*. The list field shows the angle between the three selected coordinates mapped onto the reference plane.

Note:

It is possible to save the structure list field in a file. To do this, use the Save button.

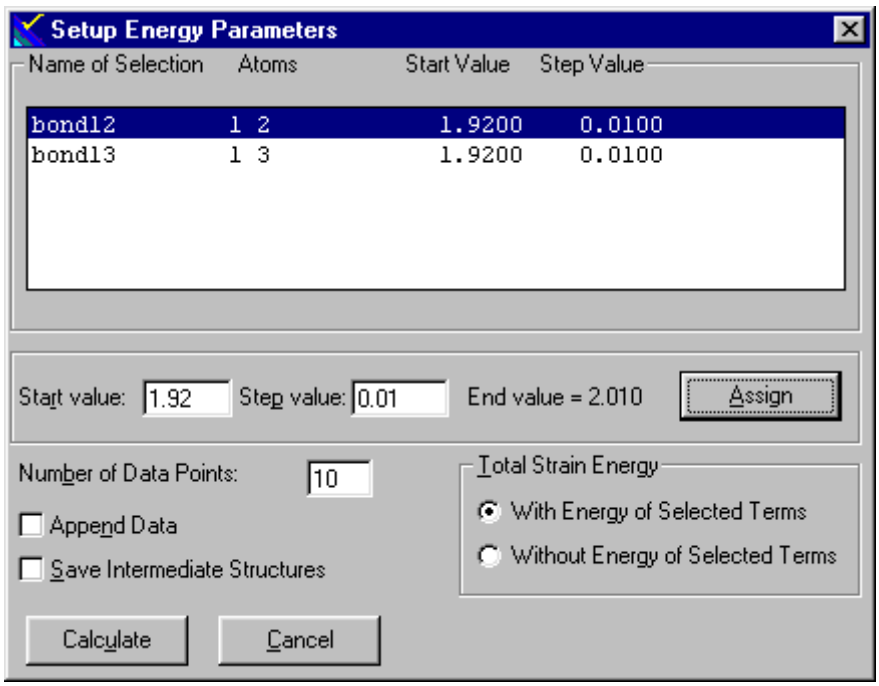
Energy

This module allows you to determine minimized structures and the corresponding strain energies as a function of up to 10 different internal coordinates (distances, valence, torsion and twist angles) each of which may be varied separately step by step. This allows you to calculate and plot the energy of an enforced modification of the shape of a molecule (e.g. torsion barrier, increasing size of the metal center, etc.). The numerical results are stored in a file and a plot of strain energy vs. value of an internal coordinate (e.g. torsion angle, bond distance) is produced and may be plotted. It is possible to modify the result file by adding additional points to the curve.

Procedure

Select a bond, an angle, a torsion angle, a twist angle or a mixture from these selections. It is recommended that this be done with menu item *Tools / Build selections* but the selections can also be defined in *HyperChem*. Save the selections and open the window *Execute / Energy*. Mark an item from the list field and choose start and step value. Don't

forget to assign the values into the list field. After you have chosen the number of calculations, you can start the energy function.

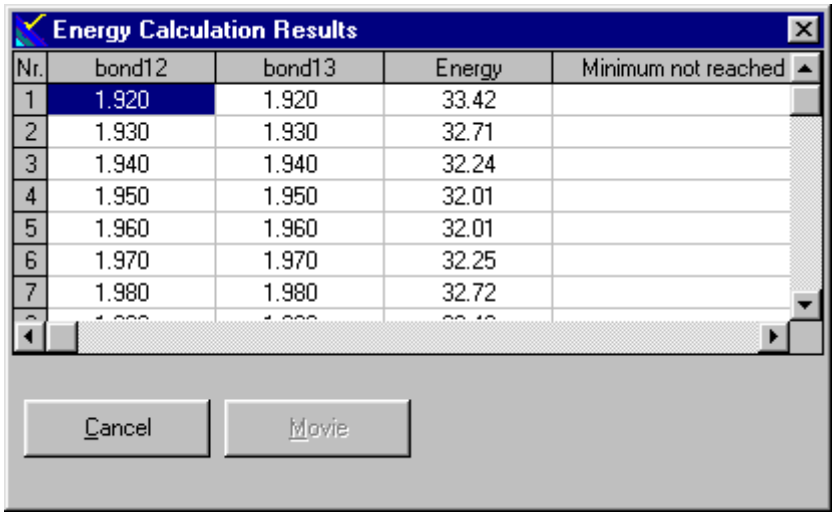


Note:

If the end value appears in red, you should reduce the step value or the number of calculations because the end value makes no sense.

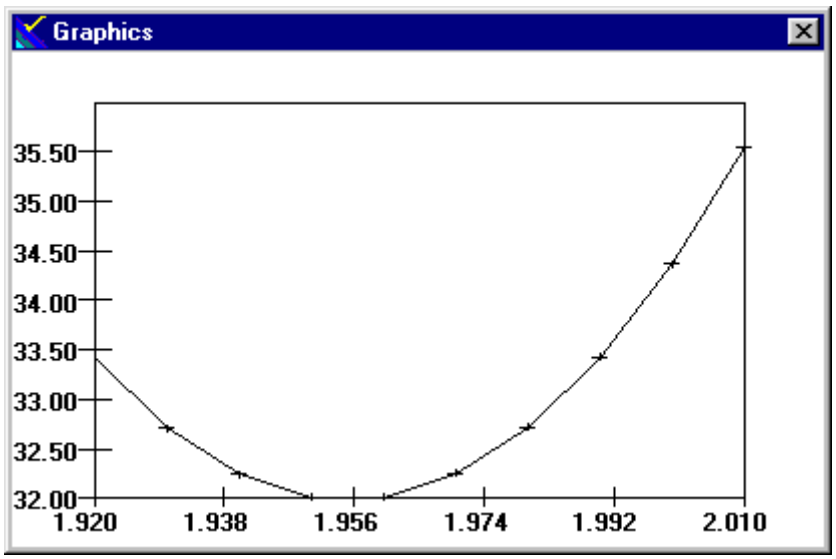
It is possible to save the intermediate structures. If your input file name is CO3.hin, and you have chosen 10 as your number of calculations, *MOMEC97* will write the intermediate structures in your output directory. The names in this example will be CO3.1, CO3.2 ⋯ CO3.10.
The window *Energy Calculation Results* shows the selected internal parameter and the energy. If the minimum was not reached in a cycle a mark will appear in the column "Minimum not reached".

You can calculate the total energy with or without the the energies of the selected interactions added to the total strain energy.



A double click with the mouse in any row shows the summary file and the corresponding structure of the row immediately. It is also possible to show all the calculated files in a movie.

The graphic window shows a plot of the energy versus internal coordinate.



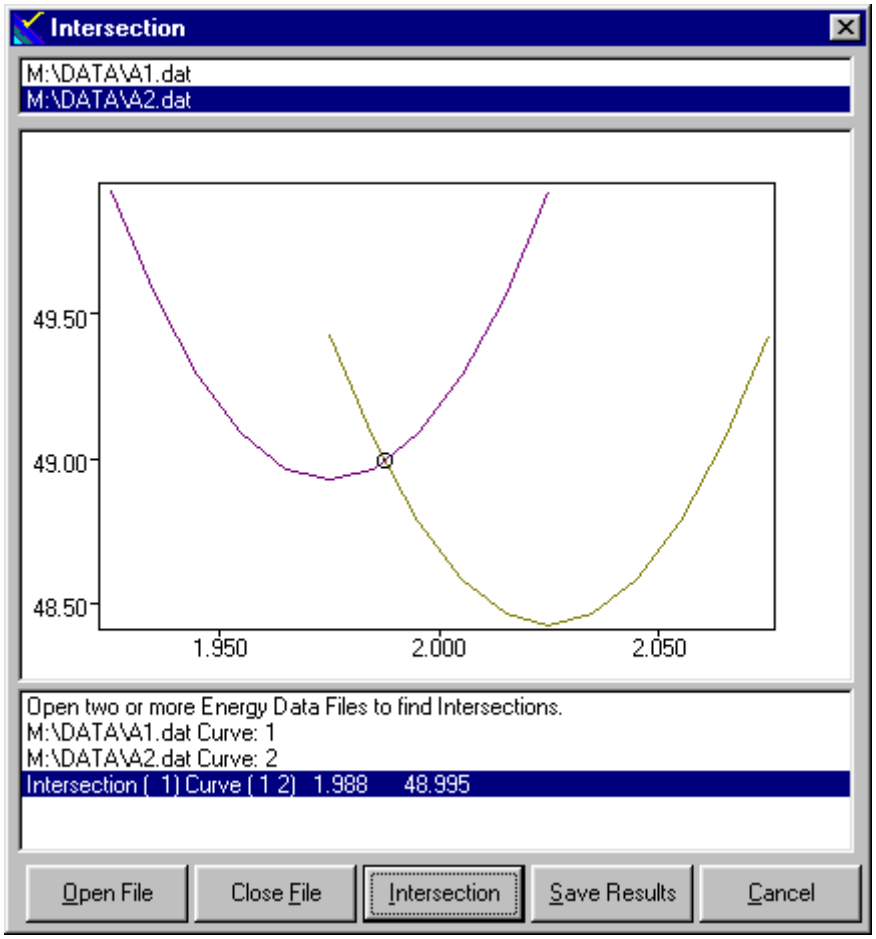
Notes:

(1) You can calculate additional points and add the results to an existing calculation. Use the option box *Append Data*.

(2) When you calculate the energy function of a twist angle, it is in some cases better to change the sign in the last box of the *Interaction Array* (see Appendix C "The Twist Angle Function"), in order to avoid getting an intermediate pyramidal structure.

Intersection

This module allows you to show curves calculated with the *Energy* or the *Jahn-Teller* modules and find all intersections of two or more curves.



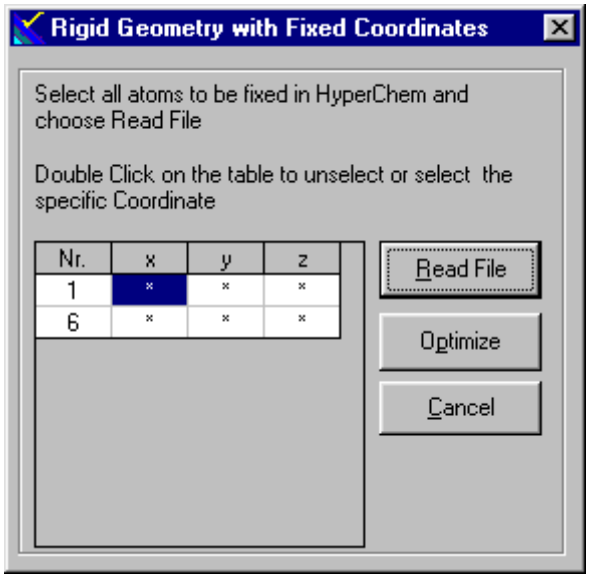
Use *Open File* to load different files with data from *Energy*. Press the *Intersection* button to calculate all intersections. When you have loaded more than two curves, *Intersection* shows you all combinations of curves (see figure above). Use the *Close File* button to close a specific file. With the *Save Results* button the results are stored in a file.

Rigid Geometry

The *Rigid Geometry* module allows you to minimize parts of a molecule while other selected parts are fixed. You may do that with constraints (see *Tools / Build Selections*). However, this is cumbersome if you want to constrain large fragments since constraints use internal coordinates, and this is also computationally inefficient. Furthermore, the maximum number of constraints is limited, and it depends on the memory size of your computer. The *Rigid Geometry* module has two options: (i) With *Fixed Atoms* you may directly select a number of atoms (up to 100) which you want to keep fixed during the refinement. Note that in *MOMEC97* this does not lead to an enhanced speed of the refinement, and the maximum number of atoms in a molecule (ca. 400 depending on the setup of your PC) includes the fixed atoms. (ii) The option *Fixed Shell* calculates a shell around the site of a molecule which you want to minimize while all atoms outside are fixed (or vice versa). Nonbonded interactions from atoms within the shell to atoms outside are included within the cutoff range. Here, the effective size of the matrices used for the minimization may be reduced enormously. Thus, the minimization is much more efficient and macromolecules may be optimized in this mode.

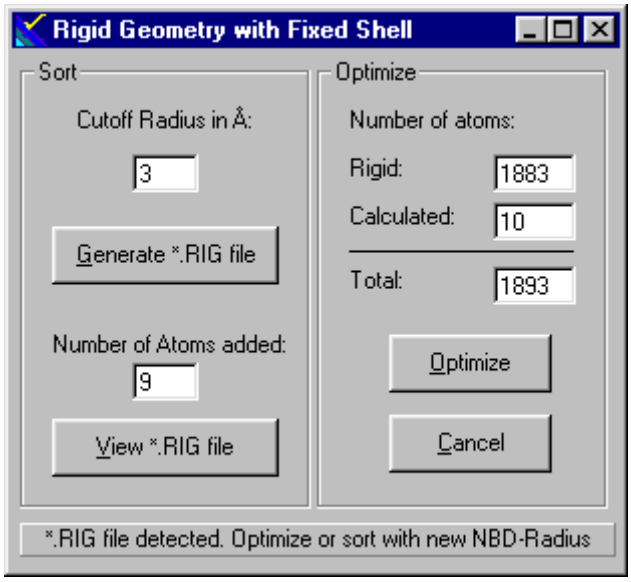
Fixed Atoms

Select the fragment of the molecule specified in *Setup / Files* that you want to keep rigid with the *Select* tool in *HyperChem*. Open the *Rigid Geometry / Fixed Atoms* window and click on the button *Read File* (this edits your Input file (*.hin or *.out), i.e. the selected atom will be saved to your file; if you want to deselect them for other applications you need to do that in *HyperChem*, i.e. deselect them with the *Select* tool and save the file or edit the *.hin or *.out file with an editor in windows). A double click on any coordinate that appears in the *Rigid Geometry with Fixed Coordinates* window changes its specification from fix to unfix and vice versa. *Optimize* uses the parameters in the *Setup / Optimization Controls* window and keeps the fragment that you have specified rigid.



Fixed Shell

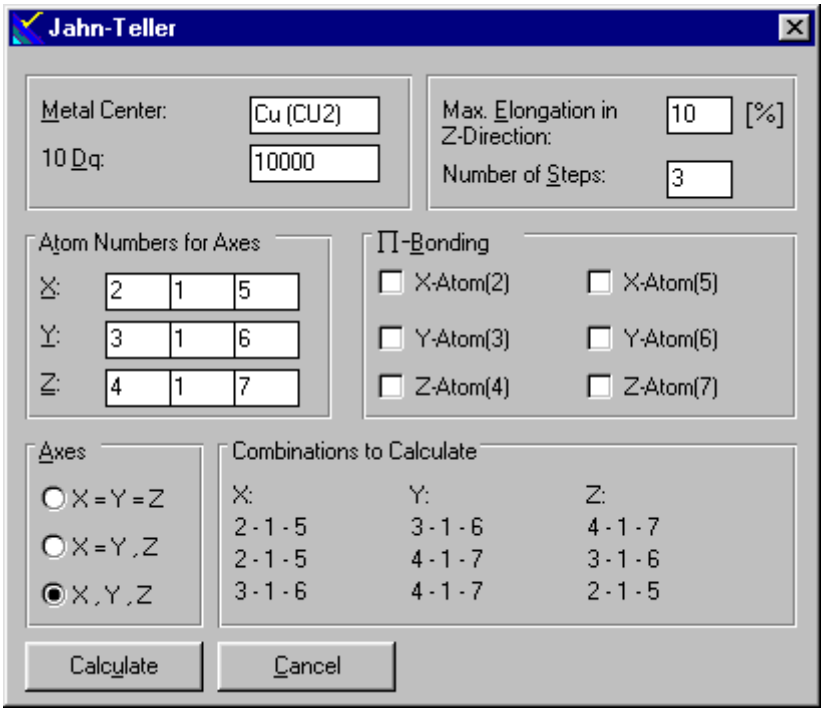
In this mode the fragment of the molecule specified in *Setup / Files*, selected in *HyperChem* will be minimized, all other atoms are fixed. *Select* all atoms of the fragment that you want to optimize (for proteins or nucleic acids you may want to use the *HyperChem* option *Select / Residues*; the *HyperChem* option *Complement Selection* is another useful tool for setting up your file). It is then necessary to save the file in *HyperChem* (*File / Save*). Next open the *Rigid Geometry / Fixed Shell* window.



Specify the *Cutoff Radius in Å* and click on *Generate *.RIG File*. This edits your Input file (*.hin or *.out, specified in *Setup / Files* in *MOMEC97*) and saves the modifications to *.rig. This file has all the information that enables *MOMEC97* to (i) fix the coordinates of all atoms that are not selected; (ii) to fix some internal coordinates in the border region between the rigid and the optimized part of the molecule to prevent distortion during the optimization process (i.e. atoms involved in a bond, valence angle or torsion to an atom in the rigid shell are fixed); (iii) select the atoms for nonbonded interactions outside the optimized shell; select the atoms that appear in the matrices used for the optimization. Execute *Generate *.RIG File* to save this file and display the number of atoms that will be used in the minimization process. *View *.RIG File* displays the selected atoms (i.e. the atoms that are optimized) in *HyperChem* and *Optimize* computes the structure with the specified parameters in *Setup / Optimization Controls*. Note, that in this mode the strain energy does not include interactions outside the calculated shell, except for the specified nonbonded interactions.

Jahn-Teller

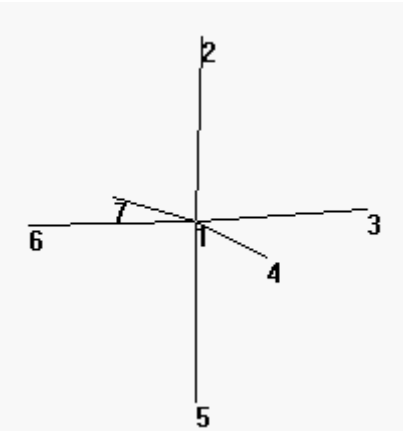
With *Jahn-Teller* you can compute tetragonally distorted octahedral structures, based on a first order harmonic approach that minimizes the sum of steric strain and electronic stabilization due to a Jahn-Teller distortion. The strain energy calculation uses the *Energy* module (see above), with the metal-donor distances following a Jahn-Teller mode (i.e. elongation of the ligands on the z-axis by 2δ and compression of the in-plane ligands by δ). The electronic term depends on the ideal metal-donor distance, the type of ligand (σ or π bonding) and the ligand field strength Δ (see Comba, P.; Zimmer, M. *Inorg. Chem.* **1994**, *33*, 5368). *Jahn-Teller* computes the optimized structure and minimum energy along the three molecular axes and the optimum overall structure is that with the lowest energy. *Execute / Jahn-Teller* opens the *Jahn-Teller* window with default values for the parameters and the definition of the axes of the molecule specified in *Setup / Files*. We recommend that you first minimize the structure in the normal mode (*Execute / Geometry Optimization*).



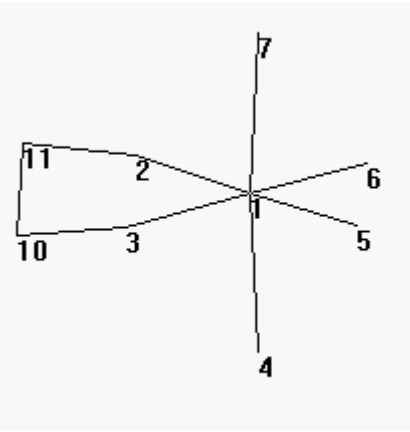
Check the *Atom Numbers for Axes* and edit if necessary. The electronic energy term is different for metal-ligand bonds that have π character. Therefore, give this information in the corresponding boxes. Also, the electronic energy depends on the ligand field strength. Thus, modify the parameter *10 Dq* if necessary. The parameters *Max. Elongation in Z-Direction* and *Number of Steps* control the stepwise calculation of the steric strain (*Energy*) and may be modified if you wish. The three options defined in the box *Axes* define whether one (X=Y=Z), two (X=Y, Z) or three (X, Y, Z) consecutive calculations are required. This depends on the symmetry of the structure.

Examples:

X = Y = Z



X = Y, Z



Calculate starts the geometry optimization. The results appear in a table:

Jahn-Teller Calculation Results

Number	Total Energy	Stain Energy	Jahn-Teller Energy		Dist 1-2	Dist 1-5	Dist 1-3	Dist 1-6	Dist 1-4	Dist 1-7
1-1	23.55	24.09	-0.54		1.945	1.945	1.945	1.945	1.975	1.975
1-2	23.12	24.20	-1.08		1.935	1.935	1.935	1.935	1.994	1.994
1-3	22.72	24.34	-1.63		1.926	1.926	1.926	1.926	2.014	2.014
1-4	22.43	24.60	-2.17		1.916	1.916	1.916	1.916	2.033	2.033
1-5	22.21	24.92	-2.71		1.906	1.906	1.906	1.906	2.053	2.053
1-6	22.07	25.33	-3.25	***	1.896	1.896	1.896	1.896	2.072	2.072
1-7	21.93	25.72	-3.80		1.887	1.887	1.887	1.887	2.092	2.092
1-8	21.95	26.29	-4.34		1.877	1.877	1.877	1.877	2.111	2.111
1-9	22.11	26.99	-4.88		1.867	1.867	1.867	1.867	2.131	2.131
1-10	22.15	27.57	-5.42	***	1.857	1.857	1.857	1.857	2.151	2.151

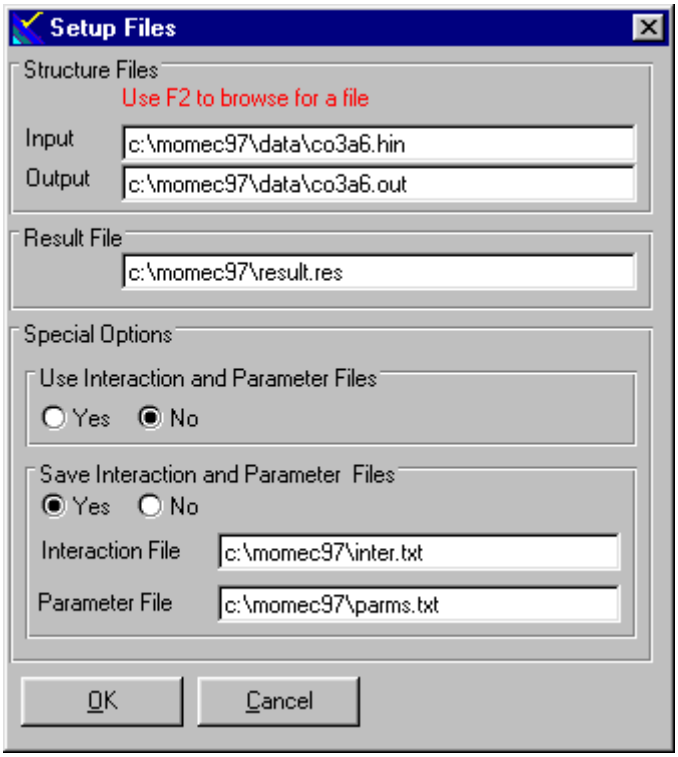
Cancel

The completed table is saved in a file and you may display the results as a curve (or as two or three curves) using *Intersection*

Setup

Files

In this window you specify the paths and names of the relevant *Input* and *Output* files are specified.

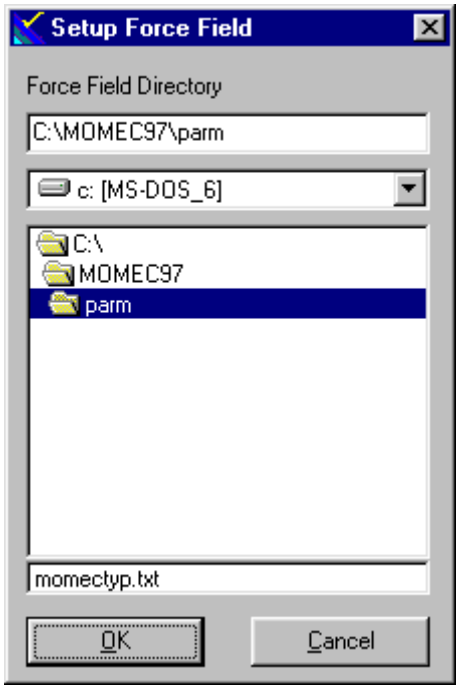


Input and *Output* are the coordinates of your initial and optimized structure, respectively, both in the *HyperChem* .hin format. With the cursor in the *Input* box you can use the F2 key to select the *Input* file from a standard dialog box. The output file will be assigned the same name but the extension *.out. The result file will has the extension *.res and a general name (e.g. momec.res) which may be changed manually (remember that this is a very long file with all the details of the refinement). If convergence was not reached (*Execute / Geometry Optimization*; *Summary File*) you may manually change the *Input* file to the corresponding *.out file to continue optimization from the prerefined file. *Use Interaction and Parameter Files* can be set to No or Yes. With "Yes" the program does not build a new interaction array, i.e. it uses the one which is specified in the *Interaction File* box. Thus, you should have created the array for the specific molecule with the menu item *Tools / Build Interactions*. This saves CPU time, and it is a useful option if you

need to optimize the same structure with different settings of the *Optimization Controls* or with different force fields (see above).

Force Field

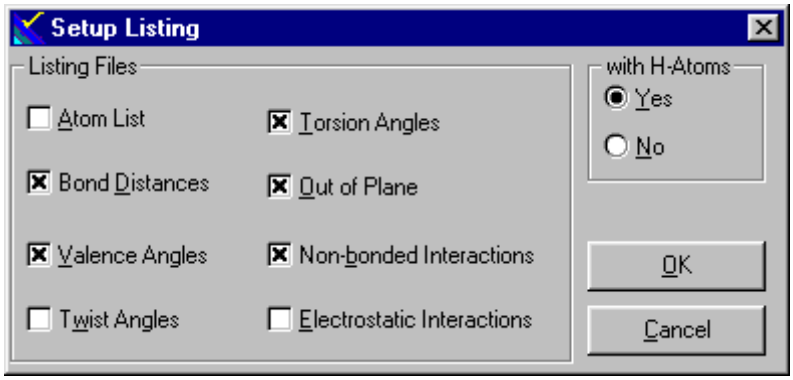
A window appears, where you can select any force field for your study.



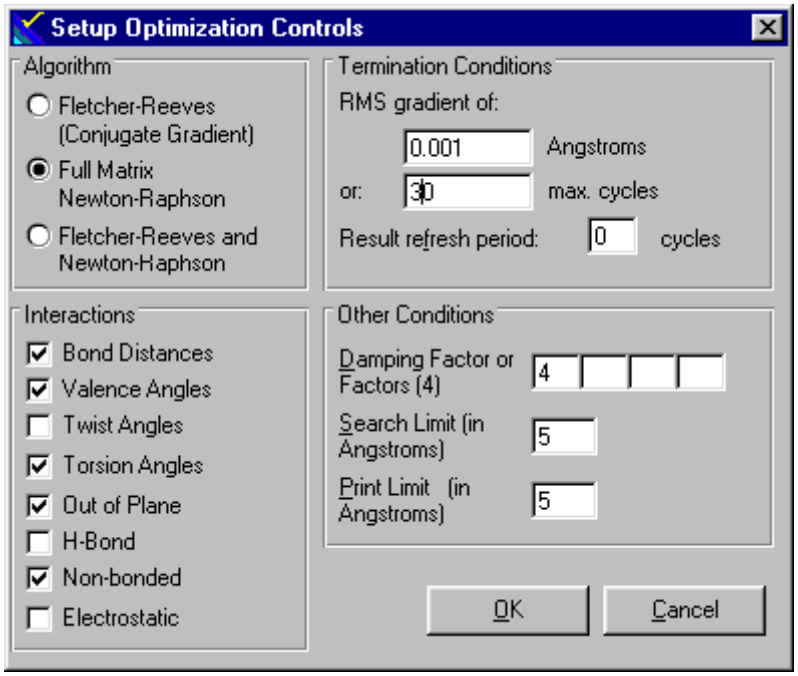
Remember that *MOMEC97* always uses the entire set of files from a single directory.

Listing

Here, you select the listing files that you want to save (see above). Make sure that the relevant potentials have been selected in *Setup / Optimization Controls*.



Optimization Controls



Algorithm

The *Fletcher-Reeves* algorithm should be used when the structure is far away from the minimum. For all other cases we recommend the use of the Full-Matrix Newton-Raphson algorithm. The Newton-Raphson minimizer must be used when you apply constraints and therefore, for all computations associated with the *Energy* and *Jahn-Teller* Modules. It is possible to begin with the Fletcher-Reeves algorithm and then finish with the Full-Matrix Newton-Raphson algorithm. When you have chosen 25

as the number of *max cycles*, the program starts first with 25 cycles (or less, if the convergence has been reached) of the Fletcher-Reeves, and then switches to the Full-Matrix Newton-Raphson minimizer (maximum of 25 cycles).

Interactions

It is possible to switch some of the potential energy functions on or off. This is not possible for *Bond Distances*, *Valence Angle* and the *Non-bonded interactions*. Switching off some potentials saves CPU time and it also allows you to quickly check the effect of some of the potentials on your molecule (another way to do that is to set a particular force constant to zero in the *Edit/View / Parameter Array* window if the option *Use Interaction and Parameter Files* in *Setup / Files* has been activated). Make sure that the terms that are relevant for your study are activated!

Termination Conditions

The program terminates when either the RMS shift is smaller than the specified value (*Convergence Reached = Yes* will appear in the *Summary File*) or when the maximum number of cycles is reached. The default value for the RMS shift is 0.001 Å.

Other Conditions

The **Damping Factor** is only used when you refine with the Newton-Raphson Algorithm. The *Damping Factor* is used when problems occur with the optimization (flat minima) or when a high energy local minimum with low barriers needs to be stabilized. The minimizer calculates a shift to the x, y and z coordinates of all atoms in your molecule, and the *Damping Factor* determines what fraction of these shifts are applied. Thus, this factor is used to reduce the speed of the refinement. There are two ways of using the *Damping Factor*: If a single value is chosen (f is an integer defined in the first of the for boxes) then all calculated shifts (d_k, $k = x_i, y_i, z_i$) are multiplied by the same factor *DAMP* ($DAMP = (1 + f \cdot d_{av})^{-1}$, where d_{av} is the mean shift, $d_{av} = \{\Sigma d_k / (3 \cdot n)\}^{½}$, n = number of atoms). Hence, large values of f lead to slow refinement and $f = 0$ leads to an undamped refinement. If four different numbers are given as damping factors, these are chosen as a function of

the steepness of the potential energy surface. f_n (n = 1, 2, 3, 4) are the four damping factors defined as integers in the four boxes. All calculated shifts d_k are multiplied by the factor $DAMP_n$ ($DAMP_n = f_n^{-1}$, and n = 1 if $20 \cdot d_{av} < 1$; n = 2 if $1 < 20 \cdot d_{av} < 2$; n = 3 if $2 < 20 \cdot d_{av} < 3$; n = 4 if $20 \cdot d_{av} \geq 4$).

The **Search Limit** value defines the cutoff distance in Å for *Non-bonded*, *Electrostatic*, and *H-bond* interactions in the calculation. The default value is 6 Å, for relatively small molecules you may use larger cutoff ranges (check the structural differences and the variation in strain energy for a simple test molecule (e.g. that of the tutorial in Appendix C) for various values of the *Search Limit*). For large molecules it may be useful to reduce the cutoff distance. For example, with a molecule of 200 atoms and a cutoff at 9 Å, about 200.000 non-bonded interactions are obtained.

The **Print Limit** value defines the cutoff distance in Å for *Non-bonded*, *Electrostatic* and *H-bond* interactions that are printed in the *Result File* and the *List Files*.

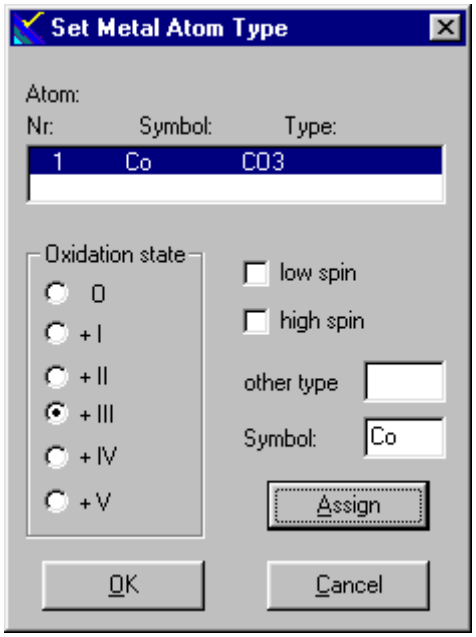
Tools

Sort Atoms

Sort Atoms rearranges the *Input* file specified in *Setup / Files*. The modified file will have the metal center, followed by the donor atoms, a second metal center (if present), followed by its donors, followed by all carbon and hetero atoms of the ligand backbone and all hydrogen atoms at the end.

Set Metal Atom Type

If you calculate a series of structures with an identical ligand sphere and different metal centers (for example the oxidized and the reduced forms of a Co(III/II) couple) you may refine one of the structures and then change the metal center by *Set Metal Atom Type*.



Edit the parameters in the window that appears, *Assign* your choice and save the file with the *OK* button. Note that this overwrites your file. Save it with a different name if you want to keep both the original and the edited files.

Delete H-Atoms

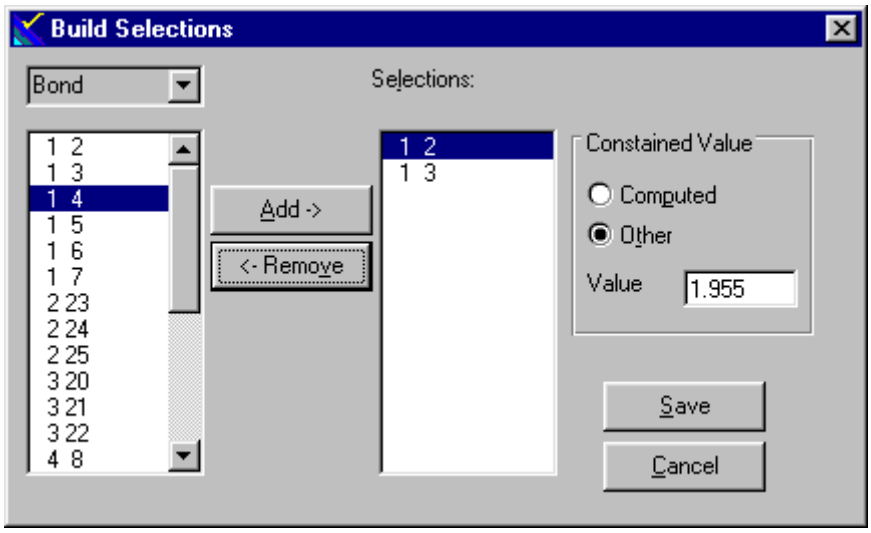
It often is useful to plot molecular structures without hydrogen atoms, and in some software packages this is a tedious job. *Delete H-atoms* is tool that saves a coordinate file without hydrogen atoms. Note that this overwrites your file (see above).

Build Interactions

Earlier in this manual we have seen that it is possible to minimize structures with existing interaction and parameter arrays, and we have seen how these may be edited. *Build Interactions* is used to build these two arrays for the structure specified in *Setup / Files*.

Build Selections

Selections for constraining internal coordinates and for *Energy* calculations may be assigned in *HyperChem*. An alternative and often preferred option is to define the selections in *MOMEC97*. *Build Selections* opens a window with a list of all *Bond*, *Angle*, *Torsion* and *Twist* interactions.



Add the internal coordinates that you want to constrain to *Selection* box and define the value to which you want it to be constrained. *Save* the file and use it in a geometry optimization (*Execute / Geometry Optimization*) or an *Energy* computation.

Delete Selections

This tool removes the selections from the input file.

Switch Atom Types

Before you use *HyperChem* for a computation (e.g. semi-empirical calculations, molecular dynamics or building molecules with the data bases available in *HyperChem*) you need to *Switch Atom Types* to the original *HyperChem* files.

- ***to MOMEC97 types***

The three files \momtypes\typerule.*mom,* \momtypes\ambertyp.*mom* and \momtypes\chem.*mom* are copied to \typerule.bin, \momtypes\ ambertyp.txt and to \chem.rul in the *HyperChem* parameter directory. Then *MOMEC97* will close *HyperChem* and start it again to activate the changes.

- ***to HyperChem types***

The three files \momtypes\typerule.*hyp,* \momtypes\ambertyp.*hyp* and \momtypes\chem.*hyp* are copied to \typerule.bin, \ambertyp.txt and to \chem.rul in the *HyperChem* parameter directory. Then *MOMEC97* will close *HyperChem* and start it again.

Appendix A: Potential Energy Functions, Force Fields, Atom Types

Potential Energy Functions

Bond stretch deformation:

$E_b = 1/2k_r(r_{ij}-r_o)^2$

r_{ij} = bond distance, k_r = force constant, r_o = ideal bond length.

Valence angle deformation:

$E_{\#\#\#} = 1/2k_{\#\#\#} (\#\#\#_{ijk}-\#\#\#_o)^2$

$\#\#\#_{ijk}$: valence angle
$k_{\#\#\#}$ = force constant, $\#\#\#_o$ = undeformed valence angle.

alternative for coordination angles
$E_{\#\#\#} = 1/2k_{\#\#\#} (\#\#\#_{ijk}-90°)^2$ if $0° \le \#\#\#_{ijk} < 135°$
$E_{\#\#\#} = 1/2k_{\#\#\#} (\#\#\#_{ijk}-180°)^2$ if $135° \le \#\#\#_{ijk} < 180°$

Twist angle deformation:

$E_{\#\#\#} = 1/2k_{\#\#\#} (\#\#\#_{ij}-\#\#\#_o)^2$

$\#\#\#_{ij}$ = angle between two planes, $k_{\#\#\#}$ = force constant, $\#\#\#_o$ = ideal twist angle.

Torsion angle deformation:

$E_{\#\#\#} = 1/2k_{\#\#\#} (1+\cos(m(\#\#\#_{ijkl} + \#\#\#_{offset}))$

$\#\#\#_{ijkl}$: torsion angle
$k_{\#\#\#}$ = force constant, m = multiplicity of the torsion,
$\#\#\#_{offset}$ = offset of optimum torsional angle

Out of plane deformation:

$E_{\#\#\#} = 1/2 k_{\#\#\#} \#\#\#_{ijkl}^2$

$k_{\#\#\#}$ = force constant, $\#\#\#_{ijkl}$ = the angle between vector jk and the plane
through ij and l.

Nonbonded interaction (also used for 1,3-interaction):

$E_{nb} = ae^{-bd_{ij}} - c*d_{ij}^{-6}$

d_{ij} is the distance between two interacting atoms and a, b and c are calculated from the van der Waals radii ($vndr_{i,j}$) and ε values as:

$a = 2014(\#\#\#_i.\#\#\#_j)^{1/2}$
$b = 12.50/vndr_i+vndr_j)$
$c = (2.25(\#\#\#_i.\#\#\#_j)^{1/2}(vndr_i+vndr_j)^6/144$

H-bond interaction:

$E_{hb} = f*d_{ij}^{-12}-g*d_{ij}^{-10}$

d_{ij} is the distance between the hydrogen donor and the hydrogen acceptor, f and g are atom based parameters

Electrostatic interaction:

$E_{\#\#\#} = q_i q_j/\#\#\# d_{ij}$

q_i and q_j are partial atomic charges in electrons
= dielectric constant (default: ### =4d_{ij}).
Electrostatic interactions are calculated only if charges are provided for atoms i and j.

Force Field Files

The default force field parameters are stored in a series of files in the directory \MOMEC97\PARM. The force field files have names of the form MOMECxxx.TXT where the letters xxx indicate what types of parameters are stored in that file. It is also possible to setup and use other force fields in other directories. Examples of entries in these files are shown here.

MOMECTYP.TXT (atom type parameters)

atom type	mass	harmonic	multiple harmonic	1,3-interaction	twist	comments
CT	12.01	1	0	0	0	C-atom
CU2	63.55	0	1	1	1	Cu-atom
CO3	58.93	0	1	1	0	Co-atom

Angles around atom type CT are calculated with the harmonic angle function; around atom type CU2 the multiple harmonic function (90° and 180°), 1,3-interactions and the twist function are used. To activate different angle functions see the menu item Edit Force Field below.

MOMECSTR.TXT (bond stretch parameters)

atom type	atom type	stretching force constant	ideal distance (Å)	comments
CT	CT	5.000	1.500	C-C bond

MOMECSTR.TXT (bond stretch parameters)

atom type	atom type	stretching force constant	ideal distance (Å)	comments
CT	CT	5.000	1.500	C-C bond

MOMECBEN.TXT (valence angle parameters)

atom type	atom type	atom type	bending force constant	ideal angle (rad)	comments

H	CT	H	0.320	1.902	H-C-H angle

MOMECTOR.TXT (torsion angle parameters)

atom type	atom type	atom type	atom type	torsion force constant	multiplicity	offset angle (rad)	comments
**	CB	N*	**	0.0112	2	1.571	**-CB-N*-**
H	CT	CT	H	0.0111	3	1.047	H-CT-CT-H

** - CB-N*-** all torsions around CB - N* have the same potential

MOMECOOP.TXT (out of plane deformation parameters)

atom type	atom type	atom type	atom type	out of plane force constant	comments
CCC	COC	COC	H	0.500	

MOMECNBD.TXT (nonbonding parameters)

atom type	van der Waals radius	ε value	comments
H	1.44	0.024	

MOMECHBD.TXT (H-bond parameters)

atom type	atom type	f-value	g-value	comments
H	NC	316.0	86.0	

MOMECTWT.TXT (twist angle parameters)

atom type	atom type	atom type	atom type	atom type	plane twist constant	ideal angle (rad)	comments
CU2	NT	NT	NT	NT	0.200	0.00	

MOMECJT1.TXT (Jahn-Teller parameters)

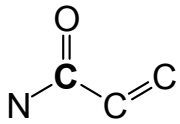
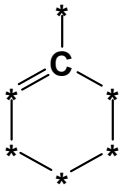
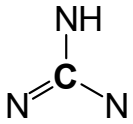
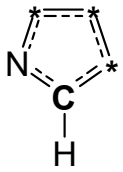
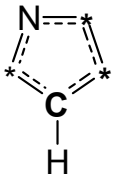
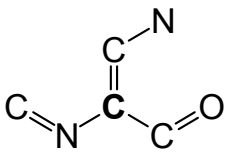
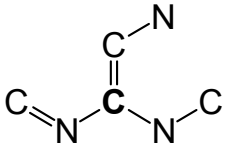
Atom type	atom type	pi-bond flag	ideal distance (Å)	comments
CU	NT	0	2.16	Cu-N bond

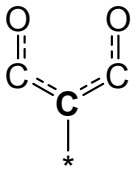
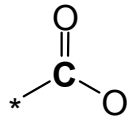
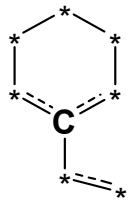
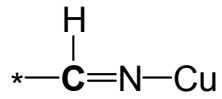
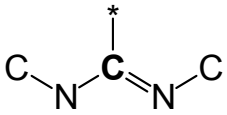
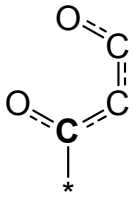
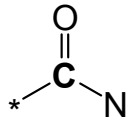
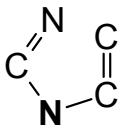
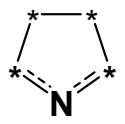
The force field parameters implemented in *MOMEC97* are published in the following papers

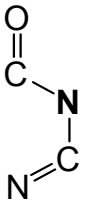
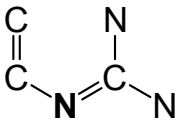
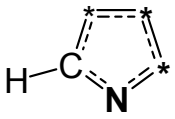
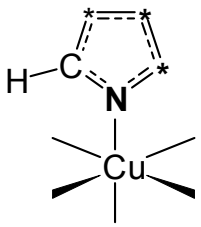
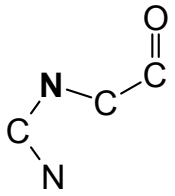
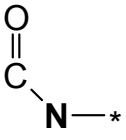
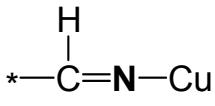
- Bernhardt, P. V.; Comba, P. *Inorg. Chem.* **1992**, *31*, 2638.
  'Molecular mechanics calculations of transition metal complexes.'
- Comba, P.; Jakob, H.; Keppler, B. K., Nuber, B. *Inorg. Chem.* **1994**, *33*, 3396.
  'Solution structures and isomer distributions of bis(ß-diketonato) complexes of titanium(IV) and cobalt(III).'
- Comba, P. *Inorg. Chem.* **1994**, *33*, 4577.
  'Prediction and interpretation of EPR spectra of low spin iron(III) complexes with the MM-AOM method.'
- Comba, P.; Zimmer, M. *Inorg. Chem.* **1994**, *33*, 5368.
  'Molecular mechanics and the Jahn-Teller effect.'
- Comba, P.; Hambley, T. W.; Ströhle, M. *Helv. Chim. Acta*, **1995**, *78*, 2042.
  'The directionality of d-orbitals and molecular mechanics calculations of octahedral transition metal compounds.'
- Comba, P.; Hambley, T.W.; Hilfenhaus, P.; Richens, D.T., *J. Chem. Soc., Dalton Trans.* **1996**, 533.
  'Solid state and solution structures of two structurally related dicopper complexes with markedly different redox properties.'
- Comba, P.; Hilfenhaus, P.; Karlin, K. D, *Inorg. Chem.* **1997**, *36*, 2309.
  'Modeling of end-on μ-peroxo dicopper(II) complexes.'
- Bol, J. E.; Buning, C.; Comba, P.; Reedijk, J.; Ströhle, M., *submitted*
  'Molecular mechanics modeling of the organic backbone of metal-free and coordinated ligands.'
- Comba, P.; Gloe, K.; Inoue, K.; Krueger, T.; Stephan, H.; Yoshizuka K. , *submitted*
  'Molecular mechanics calculations of rare earth metal complexes.'

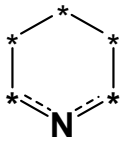
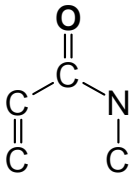
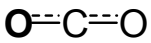
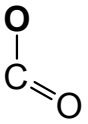
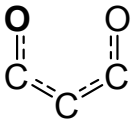
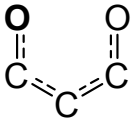
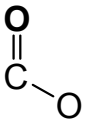
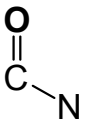
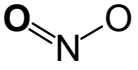
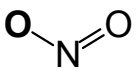
Appendix A:

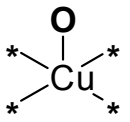
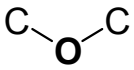
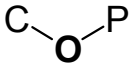
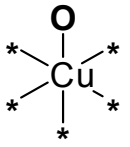
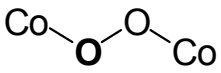
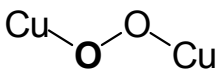
Atom types used in MOMEC97

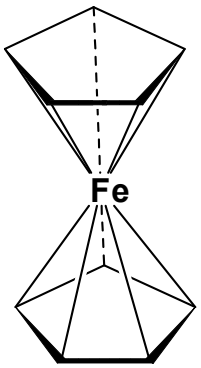
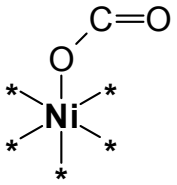
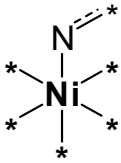
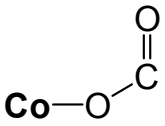
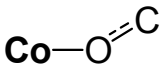
H	H	Hydrogen (default)
C		Guanine
C3		Cyanide
CA		Benzene
		Guanine
CAH		Pyrole, Imidazole
		Pyrole, Imidazole
CB		Guanine
		Guanine

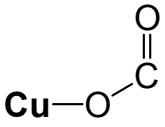
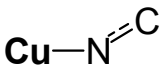
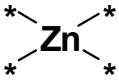
CCC		ACAC
CCO		Carboxylate
CFC		Biphenyl
CI		Imine, Cu(I)
CK		Guanine
COC		ACAC
CON		Amide
CT	**C**	Default carbon
N*		Guanine
		

N3		Cyanide
NA		Guanine
		Guanine
NAH		
NAX		axial to metal, can't set automatically
NB		Guanine
ND		Amide
NI		Imine, Cu(I)
NOO		Nitro

NP		N =(sp^2)
NT		Default
O		
O2		
OC		Carboxylate
OCC		ACAC cis
OCCT		ACAC trans
OCO		Carboxylate
		Amide
OH		
ONO		
		

OP		
OR		
OS		
OW		
	O	Oxygen (default)
OXCO		Peroxo, Co(III)
OXCU		Peroxo, Cu(II)
P	**P**	Phosphorus
SW	**S**	Sulphur (default)
TI3	**Ti**	Titanium(III)
TI4	**Ti**	Titanium(IV)
V3	**V**	Vanadium(III)
CR3	**Cr**	Chromium(III)
MN3	**Mn**	Manganese(III)
FE2H	**Fe**	high spin Iron(II)
FE2L	**Fe**	low spin Iron(II)
FE3H	**Fe**	high spin Iron(III)
FE3L	**Fe**	low spin Iron(III)

FECP		
NI2	**Ni**	Nickel(II) (default)
NI2C		Nickel(II)
NI2P		
NI2T	**Ni**	Nickel(II) (with 4 ligands)
CO2	**Co**	Cobalt(II)
CO2T		
CO3	**Co**	Default cobalt (Cobalt(III))
CO3C		Cobalt(III)
		Cobalt(III)
CU1	**Cu**	Copper(I)
CU2	**Cu**	Default copper (Copper (II))

CU2C		
CU2P		Pyridine
CU2T		
ZN2	**Zn**	Default (Zn(II))
ZN2T		
Y3	**Y**	Yttrium (III)
RH3	**Rh**	Rhodium (III)
LA3	**La**	Lanthanum (III)
CE3	**Ce**	Cerium (III)
PR3	**Pr**	Praseodymium (III)
ND3	**Nd**	Neodymium (III)
PM3	**Pm**	Promethium (III)
SM3	**Sm**	Samarium (III)
EU3	**Eu**	Europium (III)
GD3	**Gd**	Gadolinium (III)
TB3	**Tb**	Terbium (III)
DY3	**Dy**	Dysprosium (III)
HO3	**Ho**	Holmium (III)
ER3	**Er**	Erbium (III)
TM3	**Tm**	Thulium (III)
YB3	**Yb**	Ytterbium (III)
LU3	**Lu**	Lutetium (III)
PT2	**Pt**	Platinum (II)
PT4	**PT**	Platinum (IV)
U6	**U**	Uranium (III)

Appendix B:

Technical Details of the Opening Precedure of MOMEC97

The following description of the internal file transfer routine is based on the example *win.ini* file below:

[HyperChem]
Chem Parm Path=C:\HYPER

[Momec97]
MomecTypePath=C:\HYPER\MOMTYPES

HyperChem files
1. C:\HYPER\MOMTYPES\TYPERULE.HYP
2. C:\HYPER\MOMTYPES\CHEM.HYP
3. C:\HYPER\MOMTYPES\AMBERTYP.HYP

MOMEC97 files
1. C:\HYPER\MOMTYPES\TYPERULE.MOM
2. C:\HYPER\MOMTYPES\CHEM.MOM
3. C:\HYPER\MOMTYPES\AMBERTYP.MOM

When *MOMEC97* is opened the following steps will be executed automatically:

1. *MOMEC97* checks if the file CHEM.RUL is the original *HyperChem* (CHEM.HYP) file.
2. *MOMEC97* saves the files typerule.bin to c:\hyper\momtypes\typerule.hyp, chem.rul to c:\hyper\momtypes\chem.hyp and ambertyp.txt to c:\hyper\momtypes\ambertyp.hyp.
3. *MOMEC97* copies the files typerule.mom to c:\hyper\typerule.bin, hem.mom to c:\hyper\chem.rul and ambertyp.mom to c:\hyper\ambertyp.txt.

When you exit *MOMEC97* the following steps will be executed automatically:

1. MOMEC97 checks if the file CHEM.RUL is from *MOMEC97.*
2. *MOMEC97* saves the files typerule.bin to c:\hyper\momtypes\typerule.mom, chem.rul to c:\hyper\momtypes\chem.mom and ambertyp.txt to c:\hyper\momtypes\ambertyp.mom.
3. *MOMEC97* copies the files typerule.hyp to c:\hyper\momtypes\typerule.bin, chem.hyp to c:\hyper\momtypes\chem.rul and ambertyp.hyp to c:\hyper\momtypes\ambertyp.txt.

Appendix C:

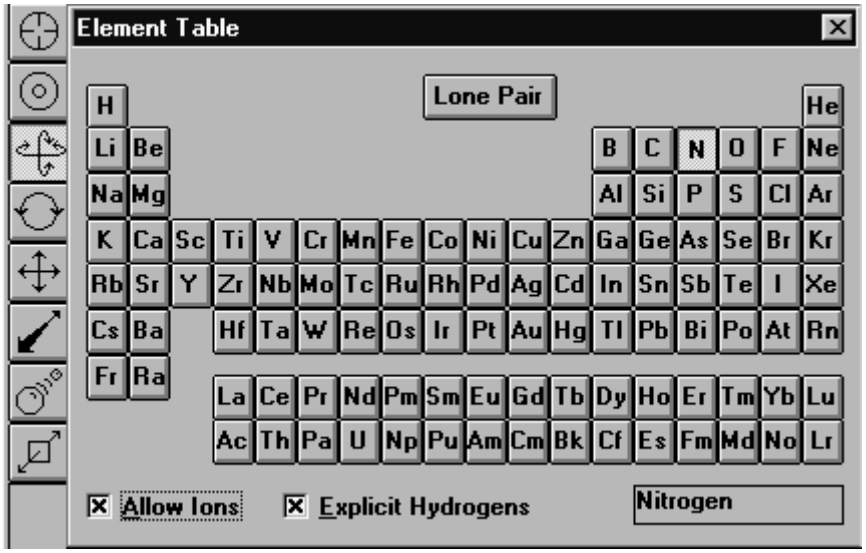
Tutorial

In the directory c:\momec\example you find the *.hin file for $[Co(NH_3)_6]^{3+}$. In this short Tutorial we describe how to build this structure using HyperChem and how to refine it using MOMEC97. A more extensive Tutorial with 24 Lessons where you can practice all relevant options of MOMEC97 is available as a separate publication (see Preface).

Building and refining a simple metal complex: $[Co(NH_3)_6]^{3+}$

Many atoms in coordination and organometallic compounds have valences that are higher than those allowed for by the standard *HyperChem* atom types. It therefore is necessary to enable the *Allow Ions* button under the *Build* menu.

Turn on the draw tool ⊕ in *HyperChem* and set the default atom to nitrogen by either double clicking on the draw tool or by selecting *Default Atom* under the *Build* menu and then choosing nitrogen from the periodic table that appears.


Element Table
Lone Pair
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Allow Ions
Explicit Hydrogens
Nitrogen

Draw six bonds starting at a common point - there is no need to worry about the geometry at this point. Note: if the *Explicit Hydrogens* option in the *Build* menu is on, this creates six hydrogen atoms and it is therefore easier if this is turned off. If not, clicking on each atom in turn will convert them to nitrogen atoms.

Set the *Default Atom* to cobalt.

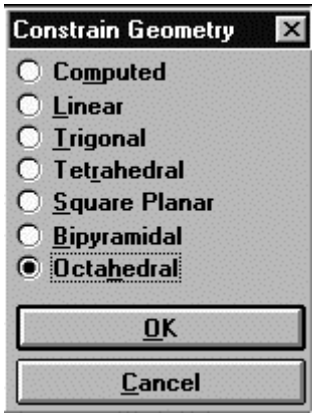
Change the central atom to cobalt by clicking on it.

Set the *Default Atom* to hydrogen.

Add three hydrogen atoms to each nitrogen atom.

Turn on the *Select* tool ◎.

Select the cobalt atom by clicking on it with the left hand mouse button, then go to the *Build* menu, choose *Constrain Geometry* and select *Octahedral*.



Deselect the cobalt atom by clicking on it with the right hand mouse button.

In the *Build* menu check that *Explicit Hydrogens* has been selected and then select the *Model Build* option.

You should now have the desired molecule. However, in *HyperChem* version 2 an error results in one of the six NH_3 groups being planar rather than tetrahedral. This can be repaired as follows:

Select the offending nitrogen atom with the *Select* tool ◎.

In the *Build* menu choose *Constrain Geometry* and select *Tetrahedral*.

Select the cobalt atom and the three hydrogen atoms attached to the planar nitrogen atom.

In the *Build* menu choose the *Model Build* option.

For the refinement of the structure it is necessary that the appropriate atom types be assigned. Therefore, check the atom types in the *HyperChem* window *Display Labels / Type*. If the *MOMEC97* types have been chosen as described earlier in this manual then the atom types will have been set correctly. If not, then select *MOMEC97* types in the *Tools* box of *MOMEC97* and the *AMBER* force field method in *the Molecular Mechanics* window under the *Setup* menu of *HyperChem*, and then choose again *Calculate Types* in the *Build* menu (you have to recompile the atom types if you have used another force field before in *HyperChem* (*Compile Type Rules* in the *Build* menu). Depending on the metal atom used it might also be necessary to assign a particular type (e.g. CO3 instead of CO2). This can be done in *HyperChem* by selecting the atom and then going to the *Set Atom Type* option under the *Build* menu or in the *Tools* menu of *MOMEC97*.

Save the structure by selecting the *Save* option under the *File* menu of *HyperChem*. When saving the file choose the path that you want to use in your *MOMEC97* calculations.

Refine the molecule with *MOMEC97: Execute / Geometry optimization*

Appendix D:

The Plane Twist Function

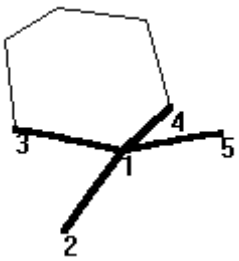
The *Twist* potential is a new potential energy function in *MOMEC97* that may be used to compute specific coordination geometries. Twist angles may also be constrained to particular values. The definition of a plane twist angle, the potential energy function, the parameterization and possible applications have been discussed in various parts of this manual. The potential may be useful not only for tetrahedral twists but also for a number of other applications. However, in the first version of *MOMEC97* the function has only been setup for tetrahedral twists, and no parameter sets have been developed and published so far. That is, we are at the very beginning of developing this field, and the setup of the function which is not yet fully optimized may change, and parameterization schemes and further applications are being developed at present.

At this stage you can use the *Plane Twist Function* to optimize four-coordinate transition metal compounds. Ligand-ligand repulsion (1,3-interactions) generally drive the geometry towards tetrahedral. The *Plane Twist* potential is therefore used to force a four-coordinate coordination compound toward square planar geometry. In a tetrahedron there are three pairs of planes with a twist angle of 90° each, and the twist potential may be assigned to all three twist angles. However, for the planar geometry there are only two sets of planes with a twist angle of 0° each. Thus, one of the angles is not used for flattening tetrahedral structures, and the two angles that are selected are those with the smallest twist angles. In the present version the default is to use only one pair of planes, i.e. that with the smallest twist angle. If you want to use two angles you need to modify the momec.ini file: Set *DefaultTwist=2* instead of *DefaultTwist=1*. You may easily check the difference between these two values since *DefaultTwist=2* will generate two sets of planes in the interaction array instead of one.

Procedure

Load the molecule, activate the *Twist Angle* in the windows *Setup / Optimization Controls, Setup / Listing* and activate the *Twist Angle* in *Edit/View / Force Field / Atom Types Parameters* for the metal center of your complex.

Build the *Interaction Array* in the *Tools* menu (*MOMEC97* generates a default order of atoms for the twist angle), check this order in the *Twist* section of the *Interaction Array*. The first value is the atom number of the metal center, followed by the two atoms that define the first plane and the two atoms that define the second plane together with the metal center. Note that the second atom in plane one (entry 3) is trans to the first atom in plane two (entry 4). Change the ordering if necessary. Do not forget to switch the option *Use Interaction and Parameter File* in *Setup / Optimization Controls* to *Yes* if you want to use edited parameter and interaction arrays.



The last entry in the *Edit/View / Interaction Array* box defines the orientation of the twist. The twist function rotates the two planes in the direction of the smallest possible movement to planarity. If the ideal angle in the example above is zero, atom 2 and 5 will turn right (figure 1). If you change the sign from the value in the last box of the *Interaction Array* from 1 to -1, you will change the orientation of the rotation (figure 2). Note that twist angles are only active with the Newton-Raphson minimizer.

figure 1

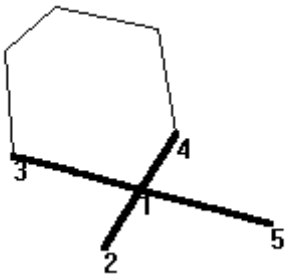
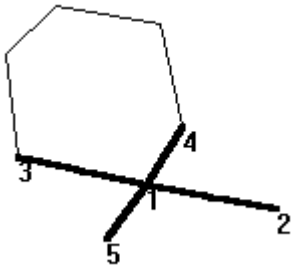


figure 2



Execute Geometry Optimization to see how the twist potential performs.